



The effect of the gas composition on hydrogen-assisted NH₃-SCR over Ag/Al₂O₃



Stefanie Tamm^{a,b}, Sebastian Fogel^{c,d}, Pär Gabrielsson^c,
Magnus Skoglundh^{a,e}, Louise Olsson^{a,b,*}

^a Competence Centre for Catalysis, Chalmers University of Technology, 412 96 Göteborg, Sweden

^b Chemical Reaction Engineering, Chalmers University of Technology, 412 96 Göteborg, Sweden

^c Haldor Topsøe A/S, Nymøllevej 55, 2800 Kgs. Lyngby, Denmark

^d Center for Individual Nanoparticle Functionality (CINF), Department of Physics, Technical University of Denmark, Fysikvej 307, 2800 Kgs. Lyngby, Denmark

^e Applied Surface Chemistry, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

ARTICLE INFO

Article history:

Received 4 October 2012

Received in revised form 25 January 2013

Accepted 28 January 2013

Available online 16 February 2013

Keywords:

Ag/Al₂O₃

H₂-effect

Reaction mechanism

Influence of gas mixture

H₂-assisted NH₃-SCR

Urea

ABSTRACT

In addition to high activity in hydrocarbon-SCR, Ag/Al₂O₃ catalysts show excellent activity for NO_x reduction for H₂-assisted NH₃-SCR already at 200 °C. Here, we study the influence of different gas compositions on the activity of a pre-sulfated 6 wt% Ag/Al₂O₃ catalyst for NO_x reduction, and oxidation of NO and NH₃. The catalyst displays high initial activity for NO_x reduction with a maximum of about 85% at 250 °C. Increasing the concentration of H₂ results in further increased NO_x reduction. Moreover, a global stoichiometry between NO:NH₃:H₂ equal to 1:1:2 is established during selective NO_x reduction conditions. When increasing the concentration of one of the reducing agents only an increase of the H₂ concentration leads to an increase in NO_x reduction, while an increase of the NH₃ concentration only is beneficial to a limit of an equimolar ratio between NO and NH₃. Under transient conditions at constant temperature, the concentration of NO reaches steady state fast, whereas it takes longer time for NH₃ due to accumulated surface species, probably on the alumina. The oxidation of NO to NO₂ is sensitive to the H₂ concentration in similarity to the SCR reaction, while higher amounts of H₂ suppress the oxidation of NH₃. Moreover, the dependency on the O₂ concentration is much higher for the NO and NH₃ oxidation than for the SCR reaction. To explain all these features a reaction mechanism is proposed in which the role of H₂ is to free silver from single oxygen atoms. Ammonia and nitric oxygen can adsorb on these sites and react probably on the border between the silver and alumina or on the alumina surface to N₂.

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1. Introduction

Fuel-efficiency in vehicles has become increasingly important owing to increasing oil prices and the concern about climate changes. A more efficient utilization of the energy in the fuel is achieved by combustion in excess oxygen. However, these conditions favor the formation of NO_x as a by-product which needs to be abated due to its negative impact on the environment. Strict emission regulations and low exhaust gas temperatures of fuel efficient engines result in a need for catalysts which can reduce NO_x in oxidizing exhausts already below 200 °C. One concept to reduce NO_x in excess oxygen is selective catalytic reduction (SCR) with either

hydrocarbons (HC-SCR) or ammonia/urea (NH₃-SCR) as reducing agent for NO_x.

Silver/alumina is known as a promising catalyst for HC-SCR and shows good catalytic activity at fairly low temperatures when small amounts of hydrogen are added as co-reductant to the feed [1,2]. One major hinder for the practical application of silver/alumina catalysts was the sensitivity to sulphur. However, recently, it was shown, that sulphur poisoned Ag/Al₂O₃ catalysts can be regenerated under conditions which are similar to those during the regeneration of a soot filter [3]. The same authors show, that the activity of an Ag/Al₂O₃ catalyst which has been exposed to sulphur stabilizes after a few exposure and regeneration cycles [3]. Moreover, they showed, that the activity of a silver/alumina catalyst can be higher after sulphur regeneration than freshly prepared [3]. The activity for NO_x reduction varies considerably with the type of hydrocarbon [4]. However, when NH₃ is used as reducing agent 90% conversion can be achieved already at 200 °C [5–7]. In contrast to HC-SCR where H₂ lowers the temperature at which the Ag/Al₂O₃ catalyst is active, Ag/Al₂O₃ is only active for NH₃-SCR in the presence of H₂. The role of this co-reductant as well as the

* Corresponding author at: Chemical Reaction Engineering, Competence Centre for Catalysis, Department of Chemical and Biological Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden. Tel.: +46 31 772 4390; fax: +46 31 772 3035.

E-mail address: Louise.Olsson@chalmers.se (L. Olsson).

mechanism for HC-SCR have been intensively investigated during the last years [2], since the addition of the reducing agent H_2 unexpectedly leads to an increase of oxidized products as observed both for hydrocarbons [1,8] and nitrogen containing species [4,5]. It has been proposed that the formation of more oxidized products is owing to a change of the state of silver. An increase of the number of small silver clusters has been observed by the addition of H_2 but even by the addition of other reducing agents [9,10]. Moreover, reduction of silver species is discussed but cannot be clearly attributed to the presence of hydrogen [11–13]. Another suggestion is that the reaction mechanism changes by the addition of H_2 , which has been exemplified by changing rates of formation and consumption of several carbon-containing intermediates [14,15]. Moreover, NH_3 is proposed to be an intermediate in HC-SCR over Ag/Al_2O_3 [16–18]. This implies, that findings on H_2 -assisted NH_3 -SCR over Ag/Al_2O_3 also are valid for HC-SCR over the same catalyst. Another area, where similarities might be expected is H_2 -SCR over precious metal catalysts [19–22]. However, a substantial difference is that silver/alumina is not active for H_2 -SCR; instead, hydrogen acts only as a co-reductant together with either NH_3 or hydrocarbons over silver/alumina catalysts. According to Burch et al. [17] different reaction mechanisms occur over precious metal-based catalysts and oxide based catalysts. One type of reaction mechanism occurs over high loaded silver/alumina catalysts and over precious metals, where substantial amounts of N_2O can be observed. Over low loaded silver/alumina catalysts, the same reaction mechanism has been proposed as over other oxide based catalysts, where the amount of formed N_2O is low.

Although silver/alumina has been studied for a long time, there are no studies available that examine the effect of varying the gas composition on the individual steps in H_2 -assisted NH_3 -SCR over Ag/Al_2O_3 , which is the objective of this work. This is performed in order to achieve fundamental insight into the reactions in this system and propose a mechanism for the H_2 effect. In order to study a highly active catalyst, which is stabilized with sulphur and thus is relevant for real applications, a pre-sulphated catalyst was used in the present study.

2. Materials and methods

Topsøe boehmite alumina was calcined at 500 °C for 2 h. The alumina was then mixed with water and a sufficient amount of $AgNO_3$ was added under intense stirring to give the desired silver loading of 6 wt%. The alumina–Ag slurry was then spray dried and calcined at 400 °C for 2 h. The catalyst was washcoated onto monolith substrate by dipping the monolith in the catalyst slurry. The substrate was a 400 cpsi cordierite monolith with a diameter and a height of 20 mm. After washcoating the monolith was calcined in flowing air at 550 °C for 2 h. The total catalyst load of the monolith was 130 g/L. After calcination the monolith was submerged in an ammonium sulfite solution (sulfite concentration = 2.8 mg/g) for ~10 s. Excess liquid was removed with pressurized air and the monolith was frozen (–30 °C). The water was then removed by sublimation in a vacuum chamber. The amount of sulfur was estimated to 0.7 wt% by weighing the monolith before and after sulfur impregnation.

The specific surface area was 270 m²/g as measured for the Ag/Al_2O_3 catalyst by N_2 -adsorption by single point BET using a Quantachrome Monosorb. The final Ag load was measured to 6.1 wt% by inductively coupled plasma – optical emission spectroscopy (ICP-OES) with a PerkinElmer Optima 3000. Results [3] show that Ag/Al_2O_3 catalysts can be activated by sulfur treatment with SO_2 in the de NO_x feed (O_2 , H_2O , NO , NH_3 and H_2). Our results (not published) show that samples also can be activated by impregnation of the catalyst with a sulfur solution (e.g. ammonium sulfite) followed by high-temperature treatment (>600 °C) in de NO_x feed.

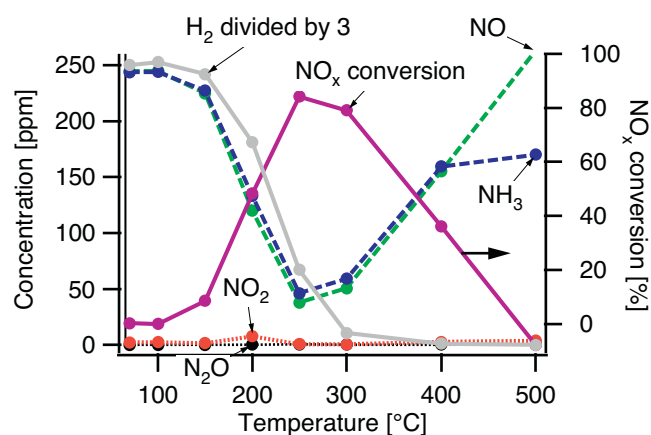


Fig. 1. NO_x conversion and outlet concentrations during H_2 -assisted NH_3 -SCR over an Ag/Al_2O_3 catalyst as a function of temperature as steady state points. Feed composition: 250 ppm NO , 250 ppm NH_3 , 750 ppm H_2 , 10% O_2 , 5% H_2O in Ar. The concentration of H_2 has been divided by 3.

The samples were freeze dried to ensure that there were no sulfur concentration gradients in the monoliths [23].

Catalytic activity tests were performed in a horizontally mounted quartz tube flow reactor. The quartz tube was 800 mm long with an inner diameter of 20 mm and was externally heated by a heating coil. The monolith was sealed against by-pass flows between the monolith and the wall of the tube with quartz wool and placed in the end of the heated zone. The temperature of the reactor was measured inside a center channel of the monolith sample and controlled 10 mm before the catalyst by a Eurotherm controller. Gases were supplied by separate mass flow controllers and water was added by a controlled evaporation and mixing system (all Bronkhorst Hi-Tech). The outlet gas composition was analyzed using a gas phase FTIR (mks-instruments, MultiGas2030) with the gas cell heated to 191 °C and by a mass spectrometer (Hiden HPR-20 QIC).

All activity tests were carried out using a total flow of 3500 ml/min, resulting in a GHSV of 33 100 h^{–1}. The fresh catalyst was first activated for 5 min at 670 °C in 5% water and then de-greened in 250 ppm NO , 250 ppm NH_3 , 10% O_2 and 5% H_2O in Ar at 600 °C for 3 h. In each subsequent experiment the sample was initially pretreated in a flow of 10% O_2 in Ar at 500 °C for 20 min. Afterwards, the catalyst was cooled in 5% water in Ar to 70 °C and exposed to the reaction mixture for 40 min. Then, the temperature was increased in 8 steps with 20 °C/min to 500 °C (100, 150, 200, 250, 300 and 400 °C). Each step lasted at least 20 min to obtain steady state conditions. Moreover, a transient experiment was performed at 200 °C, where NO , NH_3 and H_2 were switched on and off by opening and closing the respective MFC. For the evaluation, the conversion is defined as X conversion [%], which is calculated as $(1 - [X_{out}]/[X_{in}]) \times 100\%$. X consumption [ppm] is calculated as $[X_{in}] - [X_{out}]$, where X is NO_x ($NO + NO_2$), NH_3 or H_2 . Moreover, we calculated the part of NH_3 which is oxidized to NO_x during NH_3 oxidation experiments called NH_3 to NO_x as $[NO_{x,out}]/[NH_{3,in}] \times 100\%$.

3. Results and discussion

From previous studies it is known, that Ag/Al_2O_3 is active for H_2 -assisted NH_3 -SCR [5,6]. In contrast to these studies, we here use washcoated monolith catalysts.

3.1. Activity for NO_x reduction

Fig. 1 shows the conversion of NO_x between 70 and 500 °C as a function of temperature during steady state conditions and the

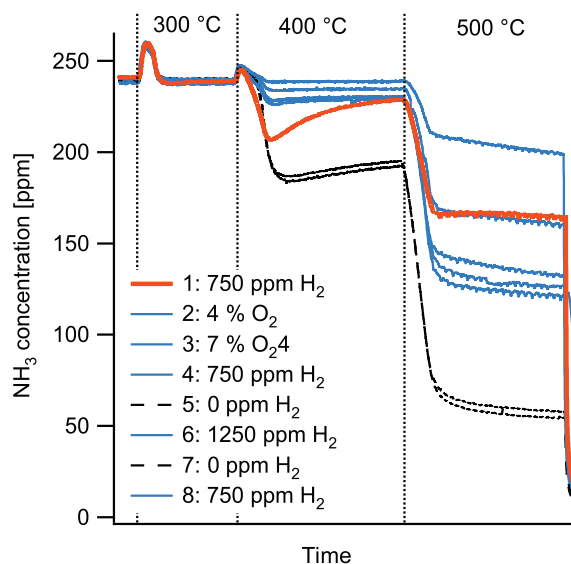


Fig. 2. Outlet concentration of NH_3 during NH_3 oxidation in different gas mixtures as a function of time while increasing the temperature stepwise from 300 to 500 °C with 20 °C/min. Base inlet gas composition: 250 ppm NH_3 , 750 ppm H_2 , 10% O_2 , 5% H_2O in Ar. Modifications are indicated in the figure. The numbers in the figure indicate the order in which the experiments were conducted.

outlet concentrations of NO , NO_2 , NH_3 , N_2O and H_2 . The NO_x conversion starts already at 150 °C and reaches a maximum of 85% at 250 °C. In accordance with Ref. [6] the selectivity to N_2 is very high which is indicated by the absence of N_2O throughout the entire temperature range. Moreover, the formation of NO_2 is very low. This is unusual for NH_3 -SCR over $\text{Ag}/\text{Al}_2\text{O}_3$ but can be attributed to the pre-sulfating of the catalyst. Hydrogen, which was shown to be essential for the reaction to occur [5], is completely consumed from 400 °C, limiting the NO_x conversion at these high temperatures. At 500 °C, significant amounts of NH_3 are unselectively oxidized to NO resulting in a negative NO_x conversion in Fig. 1.

The information of Fig. 1 is extracted from a transient experiment, where the catalyst is initially exposed to the reaction gas mixture at 70 °C. Subsequently, the temperature is increased stepwise and the increase of the temperature is accompanied by desorption of NH_3 until 250 °C (see supporting information). In parallel, the NO conversion increases and some NO_2 is initially formed already at 100 °C. From 300 °C, the NH_3 and NO concentrations increase again due to shortage of H_2 . Increasing the temperature from 400 to 500 °C causes initially a parallel increase of the NO and NH_3 concentrations until 425 °C, where oxidation of NH_3 starts causing a temporary steep decrease by 90 ppm of the NH_3 concentration accompanied by a further increase of the NO concentration. The NH_3 concentration increases thereafter again and reaches its original level after about 30 min. This transient effect is connected to the presence of NH_3 since it is not observed in NO oxidation experiments. Fig. 2 shows the NH_3 concentration during NH_3 oxidation. When heating the catalyst from 250 to 300 °C, and from 300 to 400 °C small amounts of ammonia desorb from the catalyst. At 300 °C, practically no NH_3 oxidation occurs. This observation is similar for all tested gas compositions. At 400 °C, the ammonia concentration stabilizes after the desorption peak on a stable level in most of the experiments. However, in the first NH_3 oxidation experiment conducted after an SCR experiment, the NH_3 concentration decreases rapidly followed by a slow increase during and after heating from 300 to 400 °C. A similar effect is also observed in the absence of H_2 though not as pronounced. More details of NH_3 oxidation will be discussed later. The transient effect observed between 400 and 500 °C under NH_3 -SCR conditions and

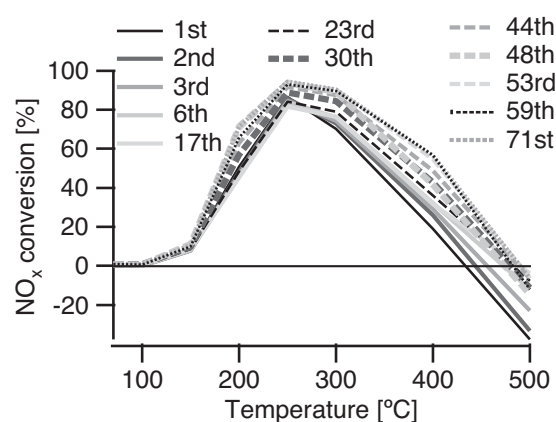


Fig. 3. NO_x conversion after aging of the catalyst with number of experiments. Feed composition: 250 ppm NO , 250 ppm NH_3 , 750 ppm H_2 , 10% O_2 , 5% H_2O in Ar.

the effect observed between 300 and 400 °C during NH_3 oxidation are quite similar. One possible explanation for this effect is a slow change in the oxidation state of Ag by a competing reaction between NH_3 and NO_2 or adsorbed NO_x . During NH_3 oxidation small amounts of NO_2 (less than 2 ppm) are formed in the absence of H_2 . However, no NO_2 was detected in the presence of more than 750 ppm H_2 . In previous studies, $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts showed good resistance against hydro-thermal treatment below 700 °C [24–26]. Although the $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst was de-greened at 600 °C in this study, it was not completely stable, and the activity for NO_x reduction improved with time. Fig. 3 shows the activity for NO_x reduction under standard conditions. This activity increased with the number of experiments where one experiment took 8 h. During the first experiments, mainly the activity for NH_3 oxidation decreased as indicated by less negative conversion at 500 °C. This effect can be explained by a loss of loosely bound sulfur, since trace amounts of SO_2 have been detected in the exhaust during the first couple of experiments. However in the following experiments, the activity for NO_x reduction increased in the entire temperature interval between 200 and 500 °C. One explanation for the improved activity could be the loss of further sulfur from the catalyst. However, after the first experiments, no SO_2 was detected in the gas phase after the catalyst. In addition, the largest changes were observed after NH_3 oxidation experiments (between the 30th and 48th experiment) in the absence of NO . After the 59th experiment, the catalyst appears to be stable. Breen et al. [24] report an increase in activity for NO_x reduction in octane-SCR after aging of an $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst at 600 °C for 16 h and attributed this to coalescing of Ag into small clusters of an average of three atoms. This effect is also reasonable in the present study. Since each experiment started by a pretreatment at 500 °C for 20 min and finished at 500 °C as the highest reaction temperature, the catalyst was in total exposed to 500 °C for more than 30 h during the course of more than 50 experiments. Another possible explanation of the increase in activity is the formation of Ag_2SO_4 , which can be expected to occur after the de-greening of the sample. Silver sulfate is reported to decrease low temperature activity [27]. During experiments the less stable Ag_2SO_4 may be converted into more stable $\text{Al}_2(\text{SO}_4)_3$ like species [28], which could explain the gain in low temperature activity.

3.2. Influence of the gas composition on the activity for NO_x reduction

Fig. 4 shows the influence of the concentration of water, oxygen, ammonia and nitric oxide on the NO_x conversion as a function of temperature. Since all the experiments shown in one graph were performed consecutively, changes due to ageing do not need to be

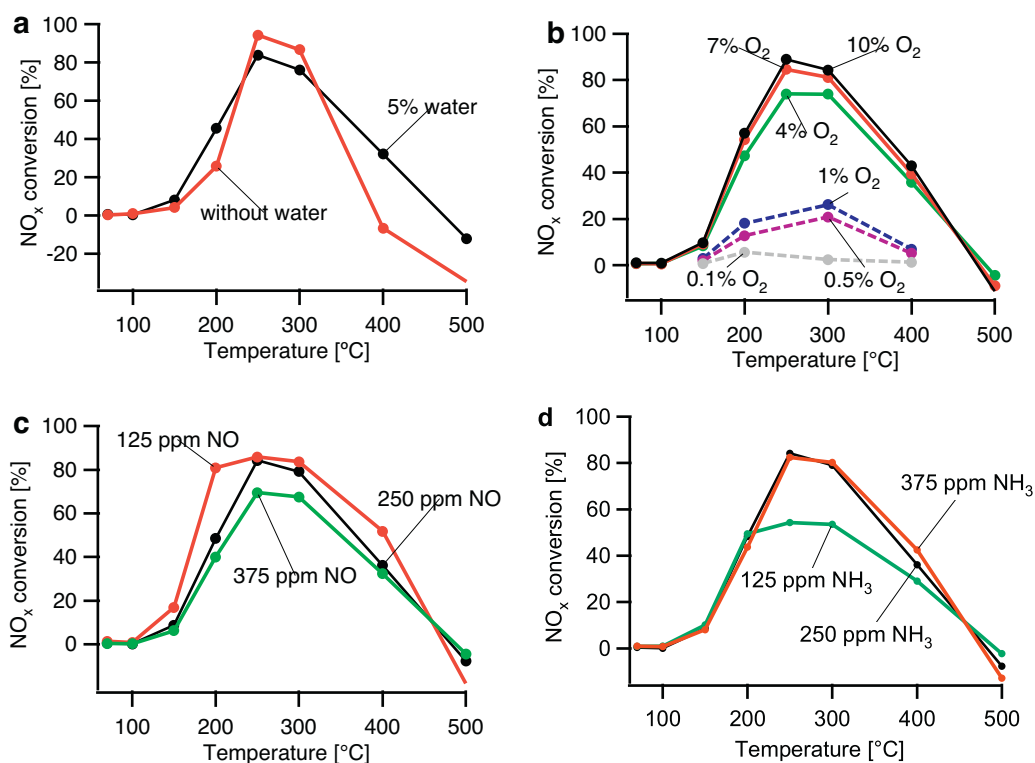


Fig. 4. Influence of the concentration of water (a), oxygen (b), NO (c) and ammonia (d) on the NO_x conversion as a function of temperature. Base inlet gas composition: 250 ppm NO, 250 ppm NH_3 , 750 ppm H_2 , 10% O_2 , 5% H_2O in Ar. Modifications are indicated in the figure.

taken into account for the interpretation. In the presence of water higher activity for NO_x reduction is observed at 200, 250 and 400 °C but the maximum conversion is somewhat lower. Moreover, less NH_3 oxidation occurs at 500 °C. However, no trend can be observed when 4 to 8% of water is present in the feed (not shown). Several roles have been proposed for water. The presence of water can reduce the amount of adsorbed NO_x and reducing agent on the catalyst due to competition of adsorption sites and thus reduce NO_x conversion [29,30]. For long hydrocarbons, this effect is beneficial, since it prevents the formation of coke and thereby increases the NO_x conversion [30]. Ammonia is known to adsorb strongly on the catalyst surface. Therefore, reduction of the amount of NH_3 could be beneficial for NO_x reduction at low temperatures, as it is the case in NH_3 -SCR over Fe-zeolites [31]. From 250 °C where the NO_x conversion is high, this effect reduces the overall NO_x reduction. Moreover, it has been proposed, that NO is activated by interaction with hydroxyl groups [32]. In the presence of water, the amount of OH-groups will be higher and could therefore contribute to a higher NO_x conversion.

Fig. 4b shows the effect of different oxygen concentrations on the activity for NO_x reduction. Even when O_2 is provided in large excess, the NO_x conversion increases with increasing of O_2 concentration. This is in accordance with previous results for HC-SCR, where it has been proposed that partial oxidation of the reducing agent (hydrocarbon) is an important part of the reaction mechanism [30,33]. In addition to the partial oxidation of hydrocarbons, partial oxidation of NO and NH_3 have been proposed as initial steps in the reaction mechanism [16,17,34]. These steps also benefit from higher O_2 concentrations. This is further supported by the very low activity with only 0.1% O_2 . Although there is still an excess of O_2 present in the feed, the NO_x conversion stays below 5%, demonstrating that O_2 is needed in the SCR reaction. With 0.5 and 1% O_2 in the feed, the maximum conversion occurs at 300 °C, which is higher than for the experiments with higher O_2 concentrations. It is

possible that at low O_2 concentrations, less H_2 is unselectively oxidized than at high O_2 concentrations and more hydrogen is thus available for the SCR reaction. Also the effect of changing the NO concentration was studied as shown in Fig. 4c. Decreasing the amount of NO in the feed gas while keeping the concentrations of all other gases constant results in an increased NO_x conversion between 150 and 400 °C. This is in accordance with previous results from HC-SCR and H_2 -assisted HC-SCR as reported in Ref. [30] and [35], respectively. At 500 °C, a negative NO_x conversion is observed. The additional NO_x is formed by oxidation of NH_3 to NO. Moreover, the sum of the NH_3 and the NO_x concentrations is about 60 ppm below the inlet values revealing that about 30 ppm N_2 is formed at 500 °C independent on the NO inlet concentration. The N_2 might be formed in the very beginning of the catalyst, where H_2 is available for NH_3 -SCR or during the oxidation of NH_3 . Since considerable amounts of N_2 are formed during NH_3 oxidation over the present catalyst (see below) the major part of the N_2 formation can be attributed to the NH_3 oxidation. Assuming that N_2 is formed during the NH_3 oxidation and this amount of formed N_2 , moreover, is independent of the NO inlet concentration indicates that NH_3 oxidation is independent of the NO concentration in the studied concentration interval.

The change in the NO_x conversion with different NH_3 concentrations is plotted in Fig. 4d. An NH_3 concentration which is significantly lower than the NO_x concentration in the feed leads to a lower NO_x conversion above 200 °C compared to the NO_x conversion with equal amounts of NO_x and NH_3 in the feed. Higher concentrations of NH_3 than NO_x in the feed, however, do not result in higher NO_x conversion. The limit in NO_x reduction seems to contradict the results in Fig. 4c on the variation of the NO_x concentration. However, in Fig. 4c the ratio of both NO to NH_3 and NO to H_2 changes, while in Fig. 4d the ratio between NH_3 to NO and NH_3 to H_2 changes. We can therefore conclude that the limit of NO_x conversion observed in Fig. 4d is caused by the ratio of NO to H_2 .

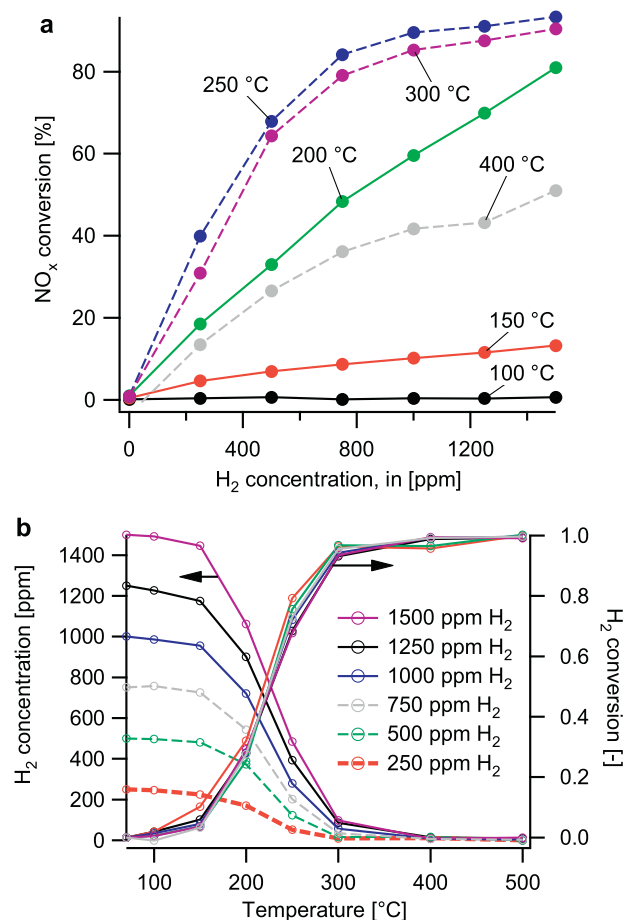


Fig. 5. (a) NO_x conversion as a function of H₂ concentration in the feed at six different temperatures in an inlet feed of 250 ppm NO, 250 ppm NH₃, 0–1500 ppm H₂, 10% O₂ and 5% H₂O in Ar. (b) Hydrogen concentration and hydrogen conversion as a function of temperature for different hydrogen concentrations in a feed gas mixture of 250 ppm NO, 250 ppm NH₃, 0–1500 ppm H₂, 10% O₂ and 5% H₂O in Ar.

The dependence of NO_x conversion on the H₂ concentration will be discussed in detail in the following section. The influence of the amount of reducing agent on the NO_x conversion has previously been studied for HC-SCR in the absence of H₂ and gave different results. A constant increase of NO_x reduction with increasing concentration of hydrocarbon was observed [33] while other groups report an increase in NO_x conversion with higher concentrations of hydrocarbons which approaches a limit at high hydrocarbon to NO ratios above certain temperatures [30,36]. This observation is in accordance with our results in Fig. 4d. Moreover, Arve et al. [35] report a higher increase in NO_x conversion with increasing hydrocarbon concentration at high than at low H₂ concentrations.

Fig. 5a shows the NO_x conversion as a function of the inlet H₂ concentration for different temperatures. Without H₂, the catalyst cannot reduce NO_x. However, with increasing H₂ feed concentration the NO_x conversion increases in the entire temperature range, in which the catalyst is active. This increase in NO_x reduction is different at different temperatures. At 250 and 300 °C, the NO_x conversion increases steeply at low H₂ concentrations and approaches slowly 90%. At both lower (150 and 200 °C) and higher (400 °C) temperatures the NO_x conversion increases continuously in the studied concentration interval. Similar trends have previously been reported for NH₃-SCR as well as HC-SCR over Ag/Al₂O₃ catalysts [4,6,35,37].

In addition to the NO_x conversion, the outlet H₂ concentration and H₂ conversion is shown as a function of temperature in Fig. 5b. Hydrogen conversion starts at 150 °C and from 400 °C complete H₂

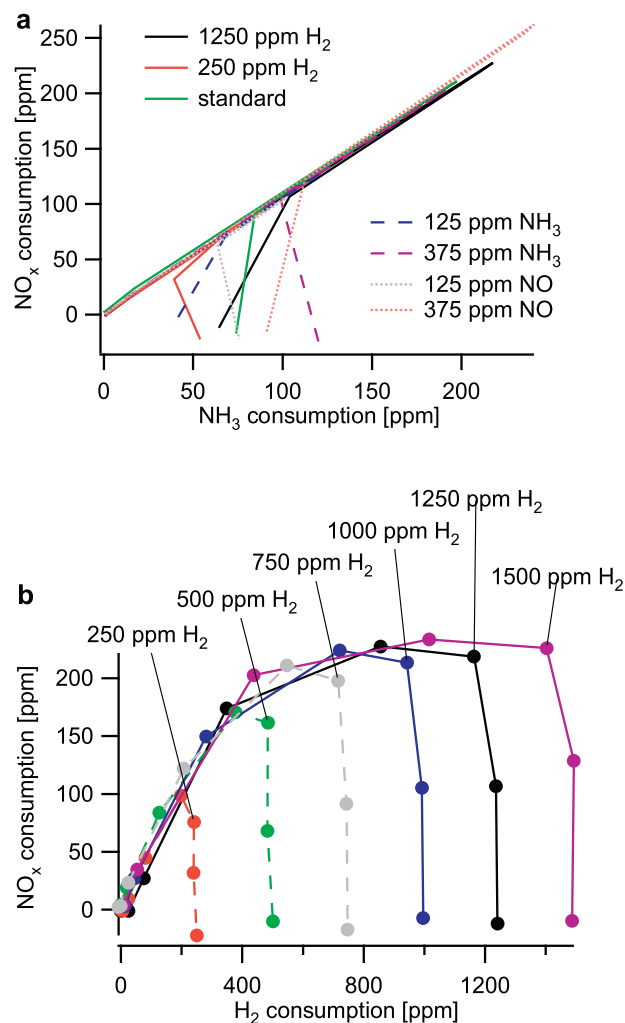


Fig. 6. (a) NO_x consumption as a function of NH₃ consumption for different gas mixtures. Standard inlet gas composition: 250 ppm NO, 250 ppm NH₃, 750 ppm H₂, 10% O₂, 5% H₂O in Ar (light grey solid line). Modifications are indicated in the figure. (b) NO_x consumption as a function of H₂ consumption in different gas mixtures. Inlet gas composition: 250 ppm NO, 250 ppm NH₃, 250–1500 ppm H₂, 10% O₂ and 5% H₂O in Ar.

conversion is seen independently of the H₂ concentration in the feed. In fact, the level of hydrogen conversion (in %) is independent of the hydrogen concentration in the feed revealing that the H₂ conversion is independent of both the NO and the NH₃ concentration. This is valid for a variation of H₂ concentrations at fixed NO and NH₃ concentrations (Fig. 5) and also for variations of the NO, NH₃ and O₂ concentrations (Fig. 4). At 300 °C, about 95% of the H₂ is converted, which might result in a shortage of H₂ in some parts of the catalyst leading to a slightly lower NO_x conversion at 300 °C compared to 250 °C. At even higher temperatures the shortage of H₂ appears to become even more severe, resulting in a clearly lower NO_x reduction. Previously it has been shown that the temperature where complete H₂ conversion is reached is shifted to lower temperatures with increasing silver loading for HC-SCR over Ag/Al₂O₃ [38]. In accordance with the present study, total H₂ conversion was achieved close to 300 °C for the most active sample [38].

In Fig. 6a the NO_x consumption at different NO (Fig. 5c) and NH₃ (Fig. 5d) feed concentrations are combined and the NO_x consumption is plotted as a function of the NH₃ consumption. This type of presentation shows, that there is a fixed molar ratio of 1:1 between NH₃ and NO conversion, which is independent of the NO, NH₃ and H₂ inlet concentrations. Only at 500 °C, where unselective

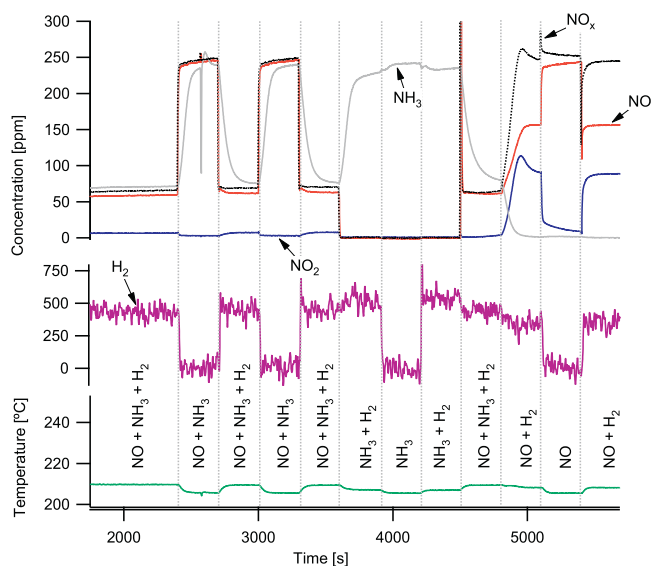


Fig. 7. Transient behavior switching off H_2 , NH_3 and NO or combinations of these gases for 5 min at 200°C under H_2 -assisted NH_3 -SCR conditions with 250 ppm NO , 250 ppm NH_3 , 750 ppm H_2 , 10% O_2 , 5% H_2O in Ar.

oxidation of NH_3 to NO takes place, this ratio is changed and the points below the main straight line are from these cases. Oxidation of NH_3 to NO results in an NO concentration, which is higher than the inlet NO concentration leading to negative NO_x conversion. Moreover, these results show that below 500°C all the converted NH_3 is exclusively involved in NO_x reduction. No loss of NH_3 by oxidation to N_2 or N_2O is observed during H_2 -assisted NH_3 -SCR below 500°C . In order to establish a ratio between H_2 and NO in the SCR reaction the NO_x consumption is plotted as a function of H_2 consumption. These results are shown in Fig. 6b. From a careful comparison of the values in Fig. 6 with Fig. 5b it is clear that below 250°C the conversion of H_2 stays below 30% and a linear correlation between NO and H_2 of 1:2 can be established. From 250°C , unselective oxidation of some H_2 occurs, indicated by a flattening of the curve in Fig. 6b. Here, the unselective oxidation of H_2 is not limiting the NO_x conversion, since the highest NO_x conversion is achieved at 250°C , where also some unselective oxidation of H_2 occurs. From 300°C , the unselective oxidation apparently leads to shortage of H_2 in some parts of the catalyst leading to a decrease in the overall NO_x reduction while the H_2 conversion is high. This feature is even more pronounced at higher temperatures. The ratio between NO and H_2 of 1:2 can be explained by assuming that the silver surface is covered by oxygen at low temperatures. This assumption is in accordance to previous results obtained by XPS [13,23]. Hydrogen removes single oxygen atoms from the silver surface freeing single sites which subsequently can be occupied by either NO or NH_3 . The adsorbed NO and NH_3 species react and form N_2 . This N_2 formation likely occurs on the interface between silver and alumina or on the alumina support, since it has been shown that Al_2O_3 plays an important role in silver/alumina catalysts [5]. Oxygen cannot re-occupy the free single sites on the silver, since it needs two sites to dissociatively adsorb on. This process is limited by the reaction of H_2 with surface oxygen. At somewhat higher temperatures, the reaction of hydrogen with the surface oxygen atoms becomes faster and there is a higher probability that two adjacent oxygen atoms are removed from the silver surface with a short time lag. These sites can be filled with oxygen disturbing the ratio between NO and H_2 of 1:2. At high temperature this process is so fast that the NO_x conversion drops due to a lack of free adsorption sites for the NO and NH_3 on the silver.

Fig. 7 shows the transient behavior of the catalyst upon fast removal of one component from the gas mixture. After reaching steady state conditions for H_2 -assisted NH_3 -SCR, H_2 is removed from the feed, rapidly halting the NO_x conversion. The NH_3 concentration starts to increase at the same time as the NO concentration. However, it takes almost 5 min for the NH_3 concentration to reach steady state after removal of H_2 . A similar behavior is observed, when H_2 is switched on again. The NO_x concentration drops immediately to steady state levels, while this takes longer time for the NH_3 concentration. The different times needed to reach steady state condition for NH_3 and NO indicate different amounts of stored surface species. Previously, we have shown that NH_x species are the predominant species during NH_3 -SCR conditions. However, the major parts of the nitrates formed on the surface are stable and will not be removed by NH_3 and H_2 [5]. In accordance with Fig. 1, some NO_2 is formed at 200°C during H_2 -assisted SCR. In the absence of H_2 , however, no NO_2 is detected. In the absence of NO , some minor NH_3 conversion occurs in the presence, but not in the absence of H_2 , indicating that the presence of H_2 even has a promoting effect on the NH_3 oxidation. This effect will be discussed later in more detail. Removing NH_3 from the feed results in oxidation of about 2/5 of the NO to NO_2 (90 ppm) at steady state. It is interesting to notice, that the NO_2 concentration increases steeply, when NH_3 is switched off and reaches its highest value just after the NH_3 concentration in the outlet has declined to zero. Thereafter, the NO_2 concentration decreases and reaches steady state levels about 5 min after the NH_3 supply has been switched off. No transient effects are observed when H_2 is added to the feed of NO , O_2 and H_2O in Ar. However, the NO_2 production increases significantly. The higher concentration of NO_2 when switching off NH_3 indicates that adsorbed parts of ammonia, like hydrogen, can have a promontory effect on the oxidation of NO to NO_2 . However, this effect is only observed when switching out NH_3 from a mixture of NO , NH_3 , H_2 , O_2 and water. A possible explanation is that the adsorbed NH_3 -fragments continue to react with the NO_x and free additional sites, on which NO can be oxidized to NO_2 . Finally, some tailing of NO_2 is observed when H_2 is removed from the above mentioned feed while NO reaches steady state more rapidly. All the discussed phenomena of the transient experiment can be explained by the previously proposed mechanism, when assuming that most of the desorbed NH_3 had been adsorbed on the Al_2O_3 . Alumina as the main NH_3 storage compound is in accordance with Ref. [39]. Moreover, the tailing of the NO_2 can be assigned to adsorbed NO species on the silver.

In summary, variation of the O_2 , NO , NH_3 and H_2 concentration in H_2 -assisted NH_3 -SCR has similar effects as in H_2 -assisted HC-SCR over Ag/Al_2O_3 catalysts. For HC-SCR over Ag/Al_2O_3 , a reaction of adsorbed NH_x species with adsorbed NO_x species has previously been proposed as a last step before N_2 formation [16,17,40,41]. This is possibly also the last step in hydrogen-assisted NH_3 -SCR over Ag/Al_2O_3 . The difference in the reaction mechanisms between NH_3 - and HC-SCR is, thus, in the formation of adsorbed NH_x species. Since a similar increase in activity is observed by adding hydrogen to the gas mixture in HC- and NH_3 -SCR, it can be assumed that H_2 promotes steps that are either common or at least similar in both reaction mechanisms.

3.3. Influence of the gas composition on the oxidation of NO and NH_3

The promotional effect of H_2 on the NO oxidation over Ag/Al_2O_3 catalysts has been shown in several studies [1,5,11,42]. Fig. 8 shows the influence of the H_2 , NO and O_2 concentrations on the NO oxidation. Similar to NO_x conversion, the oxidation of NO to NO_2 increases with increasing H_2 concentration (Fig. 8a). The shape of the NO_2 concentration in Fig. 8a resembles in shape that of the NO_x conversion during H_2 -assisted NH_3 -SCR (see supporting

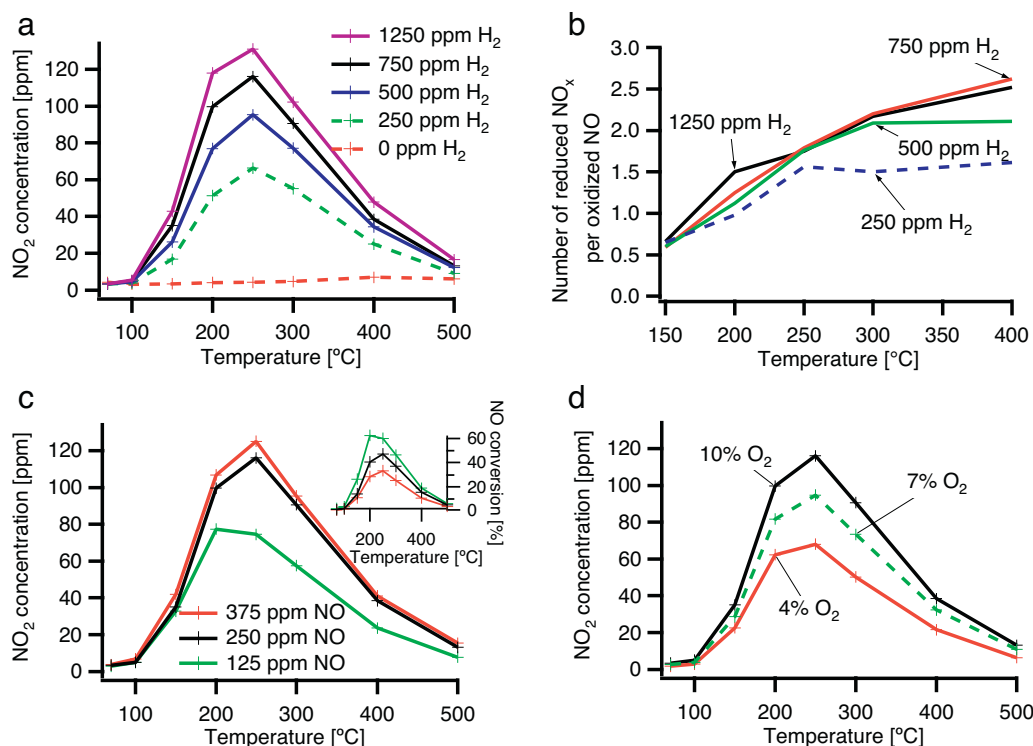


Fig. 8. NO oxidation as a function of the temperature in the presence of different amounts of H₂ (a), Ratio between reduced NO_x in SCR and NO₂ produced in NO oxidation (b), varying NO concentration (c), varying O₂ concentration (d). Base inlet gas composition: 250 ppm NO, 750 ppm H₂, 10% O₂, 5% H₂O in Ar. Modifications are indicated in the figure.

information). Therefore, the molar ratio between reduced NO_x during NH₃-SCR and oxidized NO₂ during NO oxidation was calculated for identical H₂ inlet concentrations and temperatures:

$$\frac{([\text{NO}_{x,\text{in}}] - [\text{NO}_{x,\text{out}}])_{\text{SCR conditions}}}{([\text{NO}_{2,\text{out}}])_{\text{NO oxidation}}}$$
 at fixed NO, O₂, H₂ concentrations and temperatures

In Fig. 8b these results are plotted as a function of temperature for the different H₂ inlet concentrations used. For all H₂ inlet concentrations, one mole of NO_x is reduced during SCR for two moles of NO₂ produced during NO oxidation at 150 °C. This ratio increases reaching a value of about 2.5 moles reduced NO_x per one mole formed NO₂ at 400 °C in the presence of at least 750 ppm H₂. For 250 and 500 ppm H₂, the ratio reaches limits of 1.5 and 2.1, respectively, which are observed already below 400 °C. Since more NO₂ is formed in NO oxidation than NO is reduced during SCR conditions at 150 °C, NO₂ is also expected in the outlet during NH₃-SCR. However, no NO₂ is detected, which can be explained by blocking of the active sites by NH₃ during SCR. Another explanation can be obtained from the mechanistic model proposed above. Assuming that identical concentrations of H₂ free the same amount of sites at a certain temperature NO can occupy twice as many sites during NO oxidation than during SCR, when NH₃ is present. As already stated in the discussion about Fig. 6, more sites are available at higher temperatures leading to a higher ratio of reduced NO_x during SCR to oxidized NO_x during NO oxidation.

In Fig. 8c, the effect of the NO concentration on the NO oxidation is shown. The amount of NO₂ increases as the NO concentration increases but reaches a limit at a H₂:NO ratio of 3:1 in the feed. A higher NO concentration results in the same NO₂ formation. This result is interesting since a similar limit has been observed in Fig. 4d for the influence of NH₃ on the NO_x conversion and can be interpreted as a certain amount of H₂ can only activate a certain amount of NO (probably by oxidation to NO₂) which then can be reduced by an NH₃ derived species. These results do not contradict the ratio between converted H₂:NO of 2:1 established in Fig. 6 since this ratio

is only observed for low conversions and is independent of the feed. However, also this result can be explained by H₂ freeing a certain number of sites, on which NO can adsorb. When all these sites are filled higher concentrations do not change the result.

In the insert in Fig. 8c the formation of NO₂ is shown as NO conversion in percent. This insert illustrates that conversion of NO by oxidation increases with decreasing NO concentration mainly as an effect of a higher H₂ to NO ratio. This confirms our results from Fig. 5a, where we showed that the NO_x conversion increases with higher H₂ to NO ratio. Finally, Fig. 8d demonstrates that the NO oxidation is clearly dependent on the O₂ concentration between 150 and 500 °C. This dependency is stronger than the dependency of the NH₃-SCR reaction although the NH₃-SCR reaction appears to be closely related to the oxidation of NO.

To investigate the influence of the NO₂ concentration, activity tests with equimolar amounts of NO and NO₂ as NO_x in the feed were performed (see supporting information). The NO_x reduction is only slightly higher when 50% of the NO_x is NO₂ than when all the NO_x is NO. The largest difference in NO_x conversion is observed at 200 °C were 71% NO_x conversion occurred with only NO in the feed and 85% with a mixture of NO and NO₂, corresponding to 20% higher NO_x conversion at this temperature. This result is in accordance with the study by Doronkin et al., where it was shown that Ag/Al₂O₃ is active for NH₃-SCR without H₂ providing some NO₂ in the feed [5]. Moreover without H₂, the conversion of NO_x is limited to about 30%. This limit is removed by the addition of H₂ showing that H₂ has an important role in NH₃-SCR even in the presence of NO₂ as NO_x. This observation also fits into the framework of the proposed reaction mechanism.

The activity of the catalyst for oxidation of the reducing agent is an important parameter as well. In the literature it has been shown that NH₃ can be oxidized to N₂, N₂O and NO over Ag/Al₂O₃ catalysts [5,43]. The ignition temperature and product distribution vary with the catalyst composition (e.g. Ag loading). Fig. 9 shows the NH₃

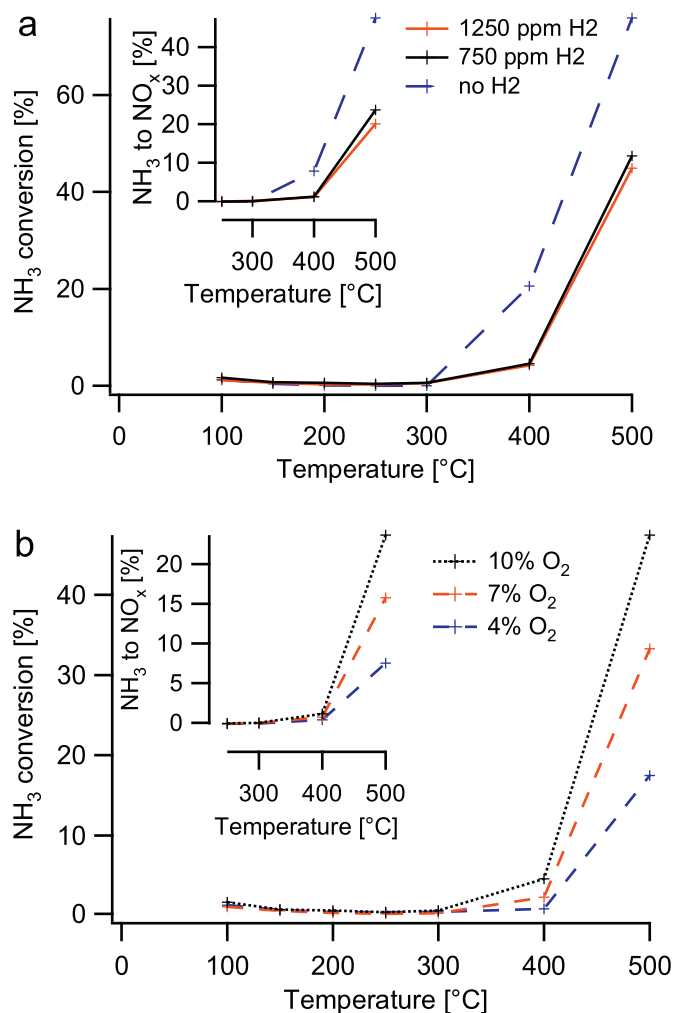


Fig. 9. NH_3 oxidation as a function of temperature in different gas mixtures. Standard gas mixture is 250 ppm NH_3 , 750 ppm H_2 , 10% O_2 and 5% H_2O in Ar. Modifications are indicated in the figure.

oxidation in different feed compositions as a function of temperature. Without H_2 , the oxidation of NH_3 starts at 400 °C and reaches 76% at 500 °C, where 48% of the NH_3 in the feed is oxidized to NO_x over the catalyst, revealing that about two thirds of the oxidized NH_3 forms NO_x and about one third N_2 (Fig. 9a). However in the presence of 750 and 1250 ppm H_2 , the oxidation of NH_3 is considerably lower, reaching about 50% at 500 °C. Moreover, only about 25% of the NH_3 in the feed is oxidized to NO_x , i.e. one half of the oxidized NH_3 forms NO_x in comparison to one third in the absence of H_2 . These results are reasonable, since NH_3 oxidation is proposed to start by the consecutive breaking of N–H bonds over $\text{Ag}/\text{Al}_2\text{O}_3$ [34]. Assuming equilibrium reaction, the presence of additional hydrogen from H_2 in the feed will shift the equilibrium to the ammonia side. Another explanation for the lower NH_3 oxidation in the presence of H_2 is that hydrogen will decrease the concentration of adsorbed oxygen, which is needed for the oxidation of NH_3 . The temperature at which NH_3 oxidation starts in the presence of H_2 is higher in Fig. 9 than expected from the transient experiment in Fig. 7, where some minor NH_3 oxidation is observed at 200 °C in the presence but not in the absence of hydrogen. These contradictory results can be explained by the fact that the catalyst changes during the first NH_3 oxidation experiment as shown in Fig. 2. Moreover, from the reaction mechanism presented above, adsorption of NH_3 also on the silver species can be expected already at 200 °C.

However, the reaction mechanism does not predict any reactions on the surface or desorption of species.

Moreover, the oxidation of NH_3 increases at higher O_2 concentrations in the feed (Fig. 9b). Similar to NO oxidation, also NH_3 oxidation is stronger dependent on the O_2 concentration than the SCR reaction. This phenomenon can be rationalized when assuming that higher NO oxidation promotes the SCR reaction while oxidation of NH_3 removes necessary compounds for the reaction. The dependence of these two conflicting effects can explain the minor dependence of the NH_3 -SCR reaction on the O_2 concentration.

4. Conclusions

The influence of different gas compositions on the activity for NO_x reduction, and oxidation of NO and NH_3 of a pre-sulfated 6 wt% $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst has experimentally been studied. It has been shown that:

- The catalyst is initially highly active for NO_x reduction with a maximum of about 85% at 250 °C. The activity increases throughout the course of the experiments due to mild aging of the catalyst at 500 °C.
- An increase in the feed concentration of hydrogen results in increased NO_x reduction. This increase is linear at 150 and 200 °C in the studied H_2 concentration interval but approaches a limit of more than 90% NO_x conversion at 250 and 300 °C.
- An increase of the NH_3 concentration is beneficial to a limit of an equimolar mixture of NO and NH_3 . A further increase of the NH_3 concentration above this ratio does not result in further improved NO_x conversion.
- A global stoichiometry between $\text{NO}:\text{NH}_3:\text{H}_2$ equal to 1:1:2 is observed during selective NO_x reduction.
- Under transient conditions at a constant temperature, the concentration of NO reaches steady state fast, whereas the stabilization of the NH_3 concentration takes longer time due to accumulation of surface species. In the presence of NH_x surface species, the concentration of NO_2 takes as long to stabilize as the NH_3 concentration and exhibits a maximum, while in the absence of NH_x surface species the NO_2 concentration stabilizes as fast as the NO concentration.
- The NO oxidation to NO_2 is sensitive to the H_2 concentration in similarity to the SCR reaction. However, the dependence on the O_2 concentration is much higher for the NO oxidation and the NH_3 oxidation than for the SCR reaction. The addition of small amounts of hydrogen during NH_3 oxidation results in decreased NH_3 oxidation and leads to a higher degree of N_2 formation.

All the observations concerning changes in the feed composition can be explained by assuming that the silver surface is covered by oxygen. Oxygen adsorbs dissociatively and competes with NO and NH_3 for the same adsorption sites. Hydrogen can remove single oxygen atoms from that surface freeing adsorption sites for NO or NH_3 . These adsorbates can react on the surface forming N_2 probably in the interface between silver and alumina or on the alumina surface. This explains the observed ratio between $\text{NO}:\text{NH}_3:\text{H}_2$ of 1:1:2 and why there is a limit to which NO_x conversion increases for the NH_3 concentration, but not for the H_2 concentration. Moreover, this reaction mechanism explains that twice as much NO_2 is formed during NO oxidation than NO is reduced during SCR at the same temperature and H_2 concentration.

Acknowledgements

This work is financially supported by the Danish Council for Strategic research and was performed at the Competence Center

for Catalysis, Chalmers University of Technology and Haldor Topsøe A/S. The collaboration with Haldor Topsøe, Amminex and DTU is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.01.064>.

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